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(54) PROCESS FOR PRODUCING GRAPHITE STRUCTURES

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing graphite structures and to structures that are suitable for use as anodes in the electrolysis of aqueous solutions.

It is known to prepare vermicular graphite by introducing an intercalating agent between the laminae of natural or synthetic graphite and expanding such treated graphite by heating. For example, a heat-expandable graphite can be prepared by contacting graphite particles of about 10 to 325 mesh (0.044—2.0 mm.) with an intercalating agent such as fuming nitric acid, fuming sulfuric acid, mixtures of concentrated nitric and sulfuric acids, or perhaloacids for a period of at least one minute. The treated graphite particles may then be washed free of excess intercalating agent and dried if desired. The resulting treated graphite is expandable by heat and, if unconfined, can be increased in volume, for example from 20 to 600 times, upon heating. Such expanded graphite is usually in light-weight particulate, vermicular, i.e. worm-like, form. Such expanded material is sufficiently light and fluffy to have a bulk density of 0.005 g/cc (grams/cubic centimeter) or even less.

Another known method of preparing vermicular graphite comprises anodically electrolyzing a natural or synthetic graphite in

an aqueous acidic or aqueous salt electrolyte at an electrolyte temperature of from 0 to 80°C. at a minimum cell potential of about 2 volts. The total quantity of electricity passed is equivalent to form 10 to 500 ampere-hours per pound (22 to 1110 ampere hours/kg.) of graphite. Electrically treated graphite, now expandable, is separated from the electrolyte solution, and heated sufficiently to cause expansion of exfoliation of the graphite flakes. The so-formed expanded graphite generally has an apparent bulk density of from 0.1 to 10 lb/ft³ (0.0015—0.16 g/cc), and preferably from 0.2 to 2 lb/ft³ (0.0032—0.032 g/cc).

It has been proposed to prepare flexible graphite foil by compressing vermicular graphite by means of pressure rollers.

The foil thus produced by uniaxial compression has anisotropic electrical and thermal properties and is useful, for example, for fabricating linings that are chemically inert at high temperature or for producing laminates.

In accordance with the present invention there is provided a process for producing a graphite structure which comprises compressing vermicular graphite, the compression being effected in at least two steps, the compression of the first step being along at least one other axis perpendicular to said first axis or at least one of said first axes.

It has now been found possible to produce unique graphite structures by compressing vermicular graphite. By the practice of the invention, it has been found possible to advantageously control the properties, including electrical and thermal conductivity, anisotropy, liquid and gas permeability, high temperature oxidation resistance, and mechanical properties, of the graphite structures.

The amount of pressure applied and the manner of pressure application is dependent on the type of formed product desired or required. In general, pressures of up to 3500 kg/cm² are employed and preferably at least 3.5 kg/cm². (All pressures given in this application are gauge pressures.) As the applied pressure is increased on the expanded vermicular graphite the bulk density of the resulting compact increases correspondingly. To illustrate, a compressed fabrication having a bulk density of from 100 to 120 lb/ft³ (1.6 to 1.92 g/cc) results at applied pressures of 4000 to 25,000 psi (280—1750 kg/cm²). It is generally preferred that the amount of pressure applied is sufficient to produce a final bulk density of from 0.3 to 2.0 g/cc.

By the method of this invention, compressed expanded vermicular graphitic structures having near-isotropic properties can be made. Such structure with reduced electrical and thermal anisotropic properties can be prepared by sequentially compressing expanded vermicular graphite, in two mutually perpendicular axes. The axis of high thermal and electrical conductivity is in a direction perpendicular to the two compression directions. The anisotropy (electrical or thermal) of these compressed graphite structures can be controlled by the pressure applied in each of the two directions during the biaxial compression. For example, if slight pressure is applied along an axis "a" and great pressure applied along an axis "b" (which is perpendicular to axis "a"), axis "c" (which is perpendicular to axes "a" and "b") would be the axis of high thermal and electrical conductivity. The minimum anisotropy would occur between the "c" and "a" axes.

The electrical and thermal conductivity values in the high conductivity direction of the compressed graphite compacts can be approximately equal to the values in the high-conductivity direction in uniaxially compressed vermicular graphite, at equal densities, but the values in the low conductivity direction of graphite sequentially compressed in two axes are usually many times more conductive than the values in the low conductivity direction of uniaxially compressed vermicular graphite. Therefore, the vermicular graphite sequentially compressed in two axes exhibits some of the characteristics of uniaxially compressed vermicular graphite without such high anisotropy in applications where high electrical or thermal anisotropy would be objectionable. In addition, the uniaxially compressed material has lower tensile strength in the direction parallel to the compression axis than in the direction normal to the compression axis. However, the graphite sequentially compressed in two

axes has a several-fold increase in tensile strength in its weak direction.

The properties of a compressed graphite structure can be made more nearly isotropic by sequentially compressing the expanded vermicular graphite along three mutually perpendicular axes, thus forming compressed dense graphite compacts which have electrical conductivity values essentially equal in all three mutually perpendicular axes (i.e. perfectly isotropic). Vermicular graphite sequentially compressed in three mutually perpendicular axes does not show the high electrical and thermal conductivities in a preferred direction and it may not show anisotropic properties, but rather may show properties close to that exhibited by commercial ("Acheson"-Process type a Registered Trade Mark) polycrystalline graphite. However, advantageously, the sequentially triaxially compressed vermicular graphite can show higher density, lower permeability, and less brittleness than synthetic "Acheson"-Process type polycrystalline graphite.

Additionally, high density bonded-expanded vermicular graphite cohered structures exhibiting marked thermal and electrical anisotropic properties and mechanical properties can be prepared in accordance with the present invention. In preparing such structures, the expanded vermicular graphite ordinarily is blended with an inorganic or organic bonding agent, ordinarily in the form of a fine powder, in an amount of from 2 to 55 weight percent and preferably from 5 to 45 weight per cent bonding agent based on the total weight of the graphite-bonder mixture.

Solid bonding agents ordinarily should be in the form of a fine powder and have a particle size of less than 100 mesh (0.149 mm.) and preferably from 200 to 325 mesh (0.074 to 0.044 mm.).

Bonding agents which ordinarily can be used in this invention are thermoplastic or thermodegradable materials and include (1) any solid organic polymer (2) organic compounds which, upon pyrolysis, yield a cementing char; and (3) inorganic glass-like bonding agents.

Examples of organic polymers suitable for use herein which are not degraded in use include polymers of ethylene, styrene, or ethylenically unsaturated chlorides, acrylic and methacrylic polymers, epoxides, polyvinyl chloride, polyesters, polyamides, polycarbonates, polyurethane resins, phenolformaldehyde resins, polyphenylene-sulphides, nylon, polytetrafluoroethylene, polyvinylidene fluoride, and copolymers of the same. These bonding agents can be used along with any required catalyst or cross-linker.

Examples of such organic char-yielding substances suitable for use herein include coal tar pitches, natural asphalts, phenol-

formaldehyde, urea-formaldehyde, polyvinylidene chloride, and copolymers containing polyvinylidene chloride, polymers of furfuryl alcohol, polyacrylonitrile, sugars, and saccharides.

Examples of inorganic glass bonding agents suitable for use herein are vitreous materials which include, glass-forming oxides such as boric oxide, silica, phosphorus pentoxide, germanium oxides, vanadium pentoxide, or other inorganic salts that can be obtained as glasses such as beryllium fluoride, and certain sulfates, chlorides and carbonates. Especially useful in this invention are those glass-formers which will "wet" the graphite such as B_2O_3 , P_2O_5 , or V_2O_5 . Commercially available glasses also are suitable as bonding agents. Typical examples of such glasses are compositions containing as an ingredient various proportions of two or more of the following oxides: silica, aluminum oxide, sodium oxide, potassium oxide, magnesium oxide, cuprous oxide, barium oxide, lead oxide, or boric oxide.

It has been found that certain inorganic compounds can be blended with expanded graphite prior to the compacting of the graphite into the desired articles, the inorganic compounds serving to increase the resistance of the graphite to high temperature oxidation. The compounds found to serve this purpose include B_2O_3 , P_2O_5 , $Ca_3(PO_4)_2$, $AlPO_4$, $Zn_3(PO_4)_2$, and $Na_2B_4O_7$. The compounds useful as oxidation-resistant additives may or may not be potential constituents of glass-forming formulations. The materials should be in a particulate form which will pass through a 100-mesh (0.149 mm.) screen and preferably a 325-mesh screen (0.044 mm.). The effective concentration of said oxidation-resistant additives generally is in the range of 0.5 to 10 weight percent of the graphite charge. At concentrations below 0.5 weight per cent the oxidation rate of the graphite article approaches that of an article of graphite alone and at concentrations above 10 weight percent there is no significant decrease in oxidation rate of the graphite and the inorganic additive may affect the physical properties of the graphite.

Liquid polymers are not usually employed as bonding agents since these can prevent formation of highly densified compositions, but may be advantageously employed when a low-density compact is desired and the liquid polymer is hardenable or curable. However, a solid polymer or other bonding agents can be dissolved in a solvent and then sprayed on the vermicular expanded graphite prior to compacting. When this technique is used to make dense compacts, the solvent is removed before compacting is attempted. Solvents suitable for use in dissolving solid polymers include, for example, xylene, kerosene, CCl_4 , and acetone.

The compressed vermicular graphite compacts have properties vastly superior to "Acheson"-Process type polycrystalline graphite. However, desirable properties of these compressed compacts such as mechanical strengths, hardness, gas and liquid impermeability can be further improved (at a slight expense of reduced electrical and thermal conductivity) by bonding the compact as described hereinbefore.

The glass-bonded compressed graphite has a particular advantage in that it overcomes temperature limitations of the polymer-bonded vermicular graphites. The polymer-bonded graphites generally undergo polymer decomposition at sustained temperatures above about 250°C. The glass-bonded composites are useful at temperatures above this limit.

However, if the product desired is to be a carbon-cemented dense vermicular graphite compact, the char yielding bonding agent-vermicular graphite blend should be baked at a temperature within the range of from 800 to 1200°C. until essentially all the volatile constituents are evolved. The ordinary range of residue carbon "cement" in such a carbon-cemented graphite structure is from about 1 to about 50 weight percent and preferably from about 5 to about 30 weight percent of the final product. Generally, as the carbon "cement" fraction decreases below about 1 weight percent, the structure resembles the unbonded compressed vermicular graphite. If the carbon "cement" content of the final product exceeds about 50 weight percent, the advantageous electrical and thermal conductivity properties of the expanded graphite fraction may be diminished.

Char-yielding bonding agents suitable for use herein include, for example, asphalt, tar, sugars, phenolformaldehyde resins. If necessary for ease of mixing and shaping, a solvent such as xylene or kerosene can be used. While compressed expanded graphite in its various forms possesses an ability to withstand high-temperature oxidation which is superior to that of almost all other forms of graphite, this characteristic may be enhanced to a remarkable degree by the addition thereto of minor proportions of oxides of boron or phosphorous or of borates and phosphates.

Articles made according to this invention find particularly good application as sealing agents, such as sealing rings, or valve packing. Such articles may or may not be prepared in such a manner as to exhibit an anisotropic conductance property. Also such articles are capable of undergoing some deformation under high compression forces without shattering or breaking, whereas articles prepared for the same purpose by using the "Acheson"-Process type crystalline

graphite or pyrolytic graphite are quite brittle and will shatter or break easily under commonly encountered deformation forces when used as packing material.

5 Graphite anodes presently employed in aqueous electrolytic processes are usually prepared by the "Acheson" process wherein coke is blended with a char-producing organic binder to yield a shaped mass, and
10 such mass is heated to above 2000°C. to decompose the organic binder and to cause graphitization. Anodes prepared in this manner are generally porous and highly susceptible to oxidation. Therefore, most of such
15 anodes are impregnated with a material such as an organic resin to improve their strength and decrease wear and oxidation rates. Such impregnated anodes still oxidize at an undesirably high rate, however, and they are very brittle and are extremely sensitive to pH. An
20 increase in pH of the aqueous solution being electrolysed rapidly increases the wear rate of the graphite anodes due to oxidation.

Accordingly, a preferred embodiment of
25 this invention provides a process for producing improved graphite structures suitable as anodes for the electrolysis of aqueous solutions. Beneficially, the process is rapid and economical and can produce a structure
30 which, when employed as an anode, is non-brittle and has greatly improved characteristics in the electrolysis of aqueous solutions.

It has now been found that an improved graphite structure suitable as an anode for
35 the electrolysis of aqueous solutions may be prepared by compressing vermicular graphite along one axis to produce a compact and then compressing the compact along an axis substantially perpendicular to the original
40 compression axis to a density of at least 1.4 g/cc. The structures thus produced have a relatively high density, are non-brittle, have high electrical conductivity, low oxidation rates, little or no porosity and show low free
45 halogen anodic overvoltages and greatly reduced sensitivity to pH of the solution being electrolysed. Each of these properties is significant in aqueous salt electrolysis, and such properties have not heretofore been obtainable in graphite anodes.

50 Preferably, the force applied along one axis to form a compact is sufficient to produce a density of from 0.2 to 1.0 g/cc. Such compact is then compressed along an axis which is at about right angles to the first compression axis with a compression force sufficient to produce a graphite density of at
55 least 1.4 g/cc and preferably a density between 1.7 and 2.0 g/cc. These densities usually can be achieved by applying pressures of from 10,000 to 20,000 psi (700—
60 1400 kg/cm²). Once the compact has been sequentially compressed along two axes to a density of about 1.4 g/cc or more, the
65 final compression to the higher density may

be accomplished by applying isostatic force. Such isostatic compression produces little or no compaction along any previously uncompacted axis. Compaction therefore continues along the axes of original compression.
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Improved mechanical properties may be imparted to such compressed vermicular graphite structures by blending solid organic or inorganic bonding agents such as hereinbefore described with the vermicular graphite prior to compression. Ordinarily, the organic or inorganic bonding agent is employed in the form of a fine powder, e.g. from 100 to 325 mesh (0.044—0.149 mm.) in an amount of from 1 weight percent to 25 weight percent, preferably from 2 weight percent to 15 weight percent. Amounts of bonding agent less than about 1 weight percent provide little or no improvement in the physical characteristics of the structure and amounts greater than about 25 weight percent may begin to adversely effect the electrical conductivity. It can be readily understood the specific density of the additive will affect the apparent bulk density of the compact. For instance, if the density of the additives is 1 g/cc, the apparent bulk density of the compact cannot as closely approach a value of 2.1 g/cc as when no additive is employed.
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Structures prepared according to this embodiment of the invention, whether or not containing a bonding agent, are useful as anodes in any of the aqueous electrolytic processes presently employing graphite anodes. These include diaphragm and mercury cells for the electrolysis of brine to produce chlorine and caustic soda, chlorate cells; bromate cells; electrolysis of NaSO₃ to produce NaOH and H₂SO₄; fluorination cells; and cells to produce hydrogen and oxygen.
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It has been found that anodes prepared in accordance herewith show anode wear rates of from 4/5 to less than 1/2 of the wear rate of the best commercially available graphite anodes in an acid medium and about 1/5 the wear rate of commercial anodes in a highly basic medium thereby indicating both a substantially reduced wear rate and a greatly decreased sensitivity to the pH of the solution being electrolysed. Likewise, the commercial electrographite used for anodes has an electrical specific resistance of about 350 microhm-inches (890 microhm-cm.) whereas anodes prepared from vermicular graphite by the process herein usually have specific resistances between about 150 microhm-inches (380 microhm-cm) and 250
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An additional advantage possessed by anodes prepared in accordance with this invention, particularly when such anodes are employed in chlorine cells, is a lower chlor-
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ine overvoltage. Improvements of as much as 200 millivolts have been found.

According to another embodiment of the invention, it has been found that a new and improved graphite structure can be prepared from a low density, expanded vermicular graphite, by first compressing such particulate vermicular graphite in one axis or radially to an increased, but still comparatively low bulk density, i.e. a bulk density of greater than 0.25 g/cc. and subsequently isostatically further compressing the relatively lightly compacted material to a relatively high apparent density, i.e. a minimum of 1.5 g/cc. A graphite structure can be thereby produced which is highly anisotropic both thermally and electrically and has improved conductivity and electrical efficiency, has low permeability to gases, and high oxidation resistance. Graphite structures produced in this manner can be made entirely of compressed vermicular graphite or may be made of a conventional electrographite core clad with an outer shell of compressed vermicular graphite.

While radial compression of vermicular graphite to a high density can produce a dense cylindrical anode having exceptionally low resistivity along the longitudinal axis, the formation of relatively large cylindrical anodes by radial compression of vermicular graphite presents serious mechanical problems due to the extremely large volume changes and high pressures required to increase the bulk density to about 1.9 g/cc. or higher. It has unexpectedly been found, however, that cylindrical anodes can be prepared which have low resistivity in the longitudinal axis by first radially compressing the vermicular graphite to a relatively light weight integral compact having a density of at least 0.25, preferably 0.5 to 0.7 g/cc, and and subsequently compressing such compact under isostatic compression to the desired higher density, e.g. to 1.5 g/cc. or above. The original radial compression effectively orients the compact in a manner such that when equal pressure is applied at all surfaces (i.e. isostatically), the compact will continue to compress and decrease in volume primarily along the axis of the vector of the original radial compression and produce a dense structure having substantially the same electrical conductivity characteristics as one which was radially compressed to the higher density.

In the first step of this process wherein the vermicular graphite is compressed into an integral structure of relatively low density, any suitable means of compression may be employed. For example, vermicular graphite may be placed in a flexible bag or sleeve which is then subjected to radial fluid pressure sufficient to produce radial compression of the compact. A pressure of from

200 to 300 psi (14—21 kg/cm²) is usually required to produce a compact having a density in the range of 0.5 to 0.7 g/cc. Usually no advantage is gained by compression at pressures above 300 psi (21 kg/cm²).

The radially compressed compact is then isostatically compressed by suitable means. A convenient procedure for isostatic compression is that commonly employed to compress ceramics and metal powders. In this method, the radially compressed compact is placed in a flexible bag or sleeve, usually made of rubber or plastics. The filled bag or sleeve is then placed in a fluid-filled autoclave and sufficient pressure is applied to produce a compact of the desired density. For use as an anode, a density of from 1.5 to 2.0 g/cc. is generally desirable. Such densities can be produced by exerting isostatic pressures on the compact of from 3500 to 50000 psi (245 to 3500 kg/cm²) with a pressure of about 20000 psi (1400 kg/cm²) being usually most practical.

After the desired density is achieved, the graphite structure may be machined to a desired tolerance or to achieve improved surface smoothness and uniformity. Even the high density compacts have a relatively low surface hardness and are easy to form or thread by machining.

Graphite structures prepared in this manner for use as anodes have a resistivity in the longitudinal direction of 140—170 microhm-inches (356—432 microhm-cm) compared to a resistivity of 250—340 microhm-inches (635—864 microhm-cm) for typical anodes made from the "Acheson" process graphite. Likewise, the anodes prepared in accordance with this process have an oxidation rate at 700°C. of only about 1/3 to about 1/2 of that found for conventional electrographite. Another striking improvement of anodes prepared in accordance with the present invention is that the permeability to helium may be only about one-millionth that of conventional graphite.

In an alternative embodiment the vermicular graphite may be first fitted or lightly compressed uniaxially to a density of from 0.015 to 0.10 g/cc prior to radial compression. Such uniaxial compression increases the resistivity of the final compact somewhat but this effect may be substantially overcome by applying higher pressure, e.g. 2000 to 20000 psi (140—1400 kg/cm²), in the radial compression step.

Substantially the same advantages can be achieved by cladding standard electrographite with compressed vermicular graphite in the same general manner as set forth hereinbefore. In one embodiment, e.g. a rod or cylinder of standard electrographite, such as "Acheson" graphite or pyrolytic graphite, is employed which is smaller in diameter than that desired for the finished anode. Such

rod or cylinder is centrally placed in a bag or sleeve, surrounded by vermicular graphite and radially compressed as previously described. The electrographite rod clad with the relatively-low-density compressed vermicular graphite is then isostatically compressed to produce a relatively high-density coating of compressed vermicular graphite directly affixed, i.e. bonded to the electrographite core. Surprisingly, in addition to the enhanced conductivity, oxidation resistances and lack of permeability, such cladding has been found to expand and contract with the core upon heating and cooling so that no rupturing occurs between the coating and the core such as is common where carbon or graphite is clad with other materials. Alternatively, such cladding may be achieved by surrounding the central rod or cylinder with rings or washers of intermediate density prepared by radial compression. Isostatic compression of the structure to a relatively high density produces a clad anode having improved characteristics. Likewise the central rod or cylinder may be wrapped with one or more layers of an intermediate density compressed vermicular graphite foil. Isostatic compression of such structure produces a clad electrode having improved conductivity and oxidation characteristics.

The most desirable proportion of cladding to electrographite core will depend on the characteristics needed and the conditions under which such anode is to be employed. At relatively low temperatures, e.g. around 700°C., a compressed vermicular graphite shell or cladding of about 1/4 inch (6.3 mm.) in thickness on a core of electrographite of 9 inches (22.8 cm.) in diameter is usually sufficient to produce an anode having significantly improved gas impermeability and oxidation resistance for extended periods of time. For longer periods of use and more severe conditions of temperature, thicker cladding or solid anodes of compressed vermicular graphite are advantageous. An increased proportion of cladding gives improved electrical and thermal conductivity and permits the anode to maintain oxidation resistance and impermeability to gases for longer periods under more severe conditions.

An additional advantage of the anodes composed of compressed vermicular graphite or clad therewith is the lack of brittleness and the increased ability to withstand shock impact. Electrographite is brittle and prone to chip and break during handling. Compressed expanded graphite, however is somewhat malleable even when highly compressed and can act as a shock absorber for encapsulated electrographite.

Once prepared as above described to the desired size and shape, an electrode having at least a surface of compressed expanded

graphite may be used in standard electrolytic methods for the production of metals such as magnesium, sodium, or steel without further modification of the equipment or the procedure. Such electrodes provide significant improvements in electrical and thermal conductivity, thermal and mechanical shock resistance, gas impermeability, and resistance to oxidation.

The following examples further illustrate the present invention.

EXAMPLE 1

A commercially available natural flake graphite having a flake size range of from 20 to 50 mesh (0.297—0.84 mm.) was wetted with a mixture of concentrated sulfuric acid and concentrated HNO₃ (weight ratio of H₂SO₄ to HNO₃ being 2:1) and then washed free of excess acid. The acidified flake was heated with a propane torch to about 1000° C. thereby producing a loose particulate worm-like product having an apparent bulk density of about 0.0032 g/cc.

The vermicular graphite was compressed at 50 psi (3.5 kg/cm²) into self-cohered blocks having an apparent density of about 0.25 g/cc. and then recompressed at right angles to the initial compression axis to a pressure of about 16000 psi (1120 kg/cm²) thereby producing a compact having an apparent density of about 1.8 g/cc.

This block was found to have specific resistances of about 1400, 606, and 150 microhm-inches (3560, 1540, and 380 microhm-cm.) in the second compression axis, first compression axis and uncompressed axis, respectively, and a maximum electrical anisotropy ratio of about 9.35 to 1.

EXAMPLE 2

Low-bulk-density expanded vermicular graphite prepared as described in Example 1 was compressed in a series of molds in three mutually perpendicular axes in the following sequence:

A. Compressed to about 30 psi (2.1 kg/cm²) to yield a compact having a density of about 0.196 g/cc.

B. Compressed at right angles to the first compression axis to a pressure of about 150 psi (10.5 kg/cm²) thereby producing a compact having a density of about 0.694 g/cc.

C. Compressing in an axis mutually perpendicular to the first and second compression axes to a pressure of about 10000 psi (700 kg/cm²) to produce a graphite block compressed along three axes having a density of about 1.72 g/cc.

The specific resistances were 630, 1260 and 1070 microhm-inches (1600, 3200, and 2720 microhm-cm.) along the first, second and third compression axes, respectively.

Thus it is seen that the maximum electrical anisotropy ratio of the thus compressed

vermicular graphite above was only about 2 to 1.

EXAMPLE 3

A set of vermicular graphite compacts was prepared from pure vermicular graphite and 15 weight percent polyethylene powder compressed to a density of 0.17 g/cc., then re-

compressing these at right angles to the first compression axis to a final pressure of 12500 psi (875 kg/cm²). The thus compressed composite containing polyethylene was fused under slight pressure at 140°C. The properties measured on these composites are listed below.

Property	Polymer-Free	15% Polymer-Bonded
Density, g/cc. ...	1.92	1.52
Specific Resistance in the uncompressed axis, Microhm-Inches ...	163	277
Microhm-Cm. ...	414	704
Electrical Anisotropy Ratio Between Uncompressed and Compressed Axis ...	2.18:1	2.60:1
Tensile Strength Parallel to High Conduction axis, Psi. ...	1700	3510
Kg/cm ² ...	118	246
Tensile Strength Parallel to Final Compression axis, (Weakest Direction), Psi. ...	42	1360
Kg/cm ² ...	2.94	95.2

EXAMPLE 4

Expanded graphite having an apparent bulk density of 0.4 pound per cubic foot (0.0064 g/cc.) was blended by tumbling, with 15 weight percent polyethylene powder (-325 mesh) (0.044 mm.). This mixture was compressed into a block having an apparent density of 0.21 g/cc., then compressed, at right angles to the first compression axis, to

a block having a density of 0.775 g/cc. Finally, the block was compressed in a direction normal to the first and second compression axes to a final density of 1.55 g/cc. (requiring a pressure of about 14000 psi (980 kg/cm²)). The block was heated to fusion temperature of the polyethylene.

The resulting composite was found to have the following specific resistances:

Parallel to the 1st compression axis → 1010 microhm-inches (2562 microhm-cm.)
 Parallel to the 2nd compression axis → 2070 microhm-inches (5250 microhm-cm.)
 Parallel to the 3rd compression axis → 816 microhm-inches (1070 microhm-cm.)

EXAMPLE 5

Vermicular graphite having a density of about 0.3 lb/ft.³ (0.0048 g/cc.) was blended with 40 weight percent pitch powder, then compressed in a mold to an approximate apparent bulk density of 0.2 g/cc. The formed compact was then rotated 90 degrees and re-compressed to about 10000 psi (700 kg/cm²) to yield a slab compressed along two axes. This slab was then pyrolysed in an oxygen-free atmosphere over an 8-day period at a maximum temperature of 950°C to yield a carbon-bonded compressed vermicular graphite slab which possessed the following properties:

1. Density = about 1.31 g/cc.
2. Specific Resistance in the Uncompressed Direction = about 231 microhm-inches (587 microhm-cm.)
3. Specific Resistance Parallel to Final Compression axis = about 948 microhm-inches (2400 microhm-cm.)
4. Electrical Anisotropy Ratio → 4.1:1
5. Tensile Strength (Parallel to Uncompressed axis) = about 1620 psi (113 kg/cm²)

6. Helium Permeability = about 1.2×10^{-3} cm²/second

EXAMPLE 6

Anode Preparation

Anode A: compressed along two axes
 Vermicular graphite of an apparent bulk density of about 0.005 g/cc. was compressed along one axis to a density of about 0.2 g/cc., then was compressed along an axis perpendicular to the first compression axis to a density of about 1.85 g/cc. The compact thus produced had a specific resistance in a direction parallel to the first compression axis of 606 microhm-inches (1540 microhm-cm.) and in a direction parallel to the uncompressed axis (i.e. the direction orthogonal to the two compression axes) of 150 microhm-inches (380 microhm-cm.).

Anode B: An Anode compressed along two axes containing an epoxy resin binder
 Vermicular graphite of an apparent bulk density of about 0.005 g/cc. was blended with fine powdery epoxy resin powder (a

heat-curable commercial epoxy formulation). The ratio of graphite to epoxy powder was 85/15 parts by weight. The blending was done by carefully tumbling the mixture so as to avoid excessive breaking-up of the vermicular graphite.

The mixture was compressed along one axis to a density of about 0.2 g/cc. and then along an axis perpendicular to the first compression axis to a density of about 1.85 g/cc.

The epoxy resin in the compact was cured by heating the compact to 400°F. (204°C.) and then it was allowed to cool.

The compact had a specific resistance in the uncompressed axis (i.e. the direction orthogonal to the two compression axis) of 226 microhm-inches (574 microhm-cm.).

Anode C: an anode compressed along two axes containing a polyethylene binder. 90 Parts of vermicular graphite of 0.005 g/cc. apparent bulk density was thoroughly blended in a tumbler with 10 parts by weight of fine powdery polyethylene (-200 mesh Standard Sieve Size) (less than 0.074 mm.). The procedure followed in making Anode B above was followed, including the 400°F. (204°C.) heat treatment.

The compact had a specific resistance in the uncompressed vector of about 200 microhm-inches (508 microhm-cm.).

Anode D: An anode compressed along two axes containing pyrolysed pitch as a binder.

The procedure followed in making Anode B above was followed, except that 15 parts by weight of a fine powdery phenol-formaldehyde resin was blended with 85 parts by weight of the vermicular graphite. The final compact had a specific resistance in the uncompressed axis of about 268 microhm-inches (680 microhm-cm.).

Anode E: An anode compressed along two axes anode containing pyrolysed pitch as a binder.

The procedure followed in making Anode

B above was followed except that 5 parts by weight of a fine powdery commercially available pitch was blended with 95 parts by weight of the vermicular graphite and the heating step was done by increasing the temperature at the rate of 8°/hour to 500°C., then heating rapidly to about 950°C., then cooling. All the heating was done with the compact in a non-oxidizing atmosphere. The heating caused pyrolysis of the pitch to yield a carbon-bonded structure.

The structure had a specific resistance in the uncompressed axis of about 161 microhm-inches (408 microhm-cm.) and a final density of 1.72 g/cc.

EXAMPLE 7

An experiment was conducted wherein three anodes of different composition were employed in diaphragm chlorine cells which were otherwise identical. The electrographite anode was a standard commercial anode made of "Acheson" process polycrystalline graphite impregnated with linseed oil. Anode A was formed by sequentially compressing vermicular graphite along two axes having a density of .185 g/cc. Anode B was composed of vermicular graphite sequentially compressed along two axes and having a density of 1.85 g/cc. and containing 15 percent by weight of epoxy resin as a binder. Such anodes were placed in laboratory-scale chlorine cells utilizing carbon cathodes and used for electrolysis of a saturated NaCl solution. The cells were operated at 75–85°C., an anolyte pH of 2.0–2.5, and an anode current density of 1 amp per square inch (0.155 ampere/cm²). Chlorine was produced at the anode and H₂ and NaOH were produced at the cathode. As necessary, H₂O, NaCl and HCl were fed to the cells to maintain electrolyte level, salinity and anolyte pH.

After 225 days of continuous operation, the anodes were removed from the cells, washed in distilled water for 72 hours, dried at 70–100°C., rewashed, redried and weighed. The anodes were found to have the following weight-loss rate:

Run	Anode Composition	Wt. Loss Rate g/day/ampere
Control	Electrographite Anode	0.030
1	Anode A	0.024
2	Anode B	0.020

EXAMPLE 8

A quantity of vermicular graphite was prepared by treating natural flake graphite with red fuming nitric acid and heating such treated flake to a temperature of about 1000°C. The vermicular graphite thus produced was a mass of worm-like particles having a bulk density of 0.005 g/cc.

A portion of the vermicular graphite thus prepared was placed in a rubber sleeve within a pressurizable vessel and the ends of the rubber sleeve were affixed in such a manner that pressure within the vessel would be exerted radially on the rubber sleeve. Water pressure of 300 psi (21 kg/cm²) was then applied within the vessel to compress the

graphite radially. The radially compressed cylinder of graphite was removed from the rubber sleeve and found to have a density of about 0.65 g/cc. Such graphite cylinder was then transferred to a sealed rubber bag, evacuated to remove the air, and placed in a pressure vessel wherein it was completely surrounded with water. Pressure within the vessel was then raised to 50000 psi (3500 kg/cm²), released, and the sealed rubber bag containing the compressed graphite was removed therefrom. Upon removal from the bag, the graphite cylinder was found to have

a density of 1.95 g/cc., an electrical resistivity in the longitudinal axis of 151 microhm-inches (384 microhm-cm.) and an electrical resistivity of about 1900 microhm-inches (4830 microhm-cm.) in the radial axis.

Such anode was heated to a temperature of 600°C. in a resistance heated tube furnace. A stream of air was continuously passed over the heated graphite and its weight was continuously monitored. Results obtained from such controlled oxidation were as follows:

	Time Min.	Sample Weight g.	Weight Loss %	Weight Loss g/minute
	0	12.420	—	—
	599	12.180	1.9	0.00040
30	1117	11.942	3.9	0.00047
	1369	11.810	4.9	0.00053
	2262	11.253	9.4	0.00062
	2337	11.203	9.8	0.00067
	2667	10.983	11.6	0.00067
35	3722	10.277	17.3	0.00067
	3847	10.190	18.0	0.00069
	4919	9.364	24.6	0.00068
	5424	9.016	27.4	0.00069
	6365	8.294	33.4	0.00077

As a comparison, a cylinder of commercially available electrographite 1/2 inch (12.7 mm.) in diameter and 2 inches (50.8 mm.) in length was likewise oxidized in the same furnace and under the same conditions. This

electrographite cylinder had a specific resistivity of about 280 microhm-inches (710 microhm-cm.) and a density of 1.67 g/cc. The results obtained were as follows:

	Time Min.	Sample Weight g.	Weight Loss %	Weight Loss g/minute
	0	10.126	—	—
	900	8.648	14.6	0.00164
	1140	8.054	20.4	0.00247
	1200	7.904	22.0	0.00249
55	1345	7.541	25.6	0.00252
	1675	6.744	33.4	0.00242

These results show that the weight loss due to oxidation of the anode of this invention is only about 1/6 that of conventional electrographite.

In the same manner, a portion of the vermicular graphite was radially compressed into cylindrical shape under a force of 250 psi (17.5 kg/cm²) and then isostatically compressed under a pressure of 30000 psi (2100 kg/cm²). The compressed graphite cylinder produced thereby had a density of 1.86 g/cm³ and an electrical resistivity of 169 microhm-inches (430 microhm-cm.). When tested for oxidation rate by the above method, substantially the same results were obtained as with the compressed vermicular graphite anode above.

EXAMPLE 9

An additional portion of the expanded low density vermicular graphite prepared in Example 10 was placed in a wooden mold having a cross-section of 1.25 inches×4.625 inches (3.2×11.8 cm.) and compressed uniaxially to a density of 0.60 g/cc. The compact thus produced was placed in a sealed rubber bag and evacuated to remove the air therefrom. The rubber bag was then subjected to an isostatic hydrostatic pressure of 50000 psi (3500 kg/cm²) and the compacted graphite was found to have a density of 1.93 g/cc., an electrical resistivity along the axis of original compression of about 24800 microhm-inches (63000 microhm-cm.) and

an electrical resistivity along the axis at right angles to the axis of original compression of 161 microhm-inches (408 microhm-cm.).

EXAMPLE 10

5 In a manner similar to Example 10, natural flake graphite was treated with an acid mixture containing 85 percent by weight concentrated sulfuric acid and 15 percent by weight concentrated nitric acid. The acid-treated flakes were then heat expanded in a methane flame at a temperature of about 1000°C. to produce vermicular graphite having a bulk density of about 0.005 g/cc.

10 A portion of the vermicular graphite thus produced was radially compressed, in the same manner as Example 10, to a density of 0.26 g/cc. The compact thus produced was then heated to 1450°C. under vacuum for 45 minutes to remove any residual acid contained therein, and then isostatically compressed in the manner of Example 10 to a pressure of 50000 psi (3500 kg/cm²) to form a cylindrical graphite rod.

15 The compressed vermicular graphite rod thus produced was then employed as the anode in an electric furnace. A standard graphite crucible acted as the furnace shell and as the cathode. To such crucible was added 100 g. of steel scrap and current was passed between the anode and cathode until a pool of molten steel was obtained. Weighing of the compressed vermicular graphite anode before and after use showed a weight loss due to arc erosion and oxidation equivalent of 1.5 g. of graphite/kg. of steel. This compares to accepted commercial losses of 4.5 to 6.5 g. of electrographite per kg. of steel.

EXAMPLE 11

20 Another portion of the vermicular graphite prepared in Example 12 was applied as cladding to a 9 inch (22.8 cm.) diameter cylinder of electrographite. Rings of compressed vermicular graphite were prepared in a circular mold having a centrally located circular pin to provide an annular space with an inside diameter of 9 inches (22.8 cm.) and an outside diameter of 18 inches (45.6 cm.). Such mold was filled with vermicular graphite and compression applied with a metal ring piston having the same inside and outside dimensions as the annular space. Sufficient pressure was applied to the vermicular graphite to produce rings having a thickness of 6 inches (15 cm.) and a density of 0.05 g/cc. The rings were removed from the pin and an electrographite cylinder having a 9 inch (22.8 cm.) diameter was inserted into a stack of 10 of such low density rings. 25 The composite graphite cylinder thus prepared was then radially compressed under a pressure of 300 psi (21 kg/cm²) to compress the cladding to a density of 0.6 g/cc. Such clad cylinder was then isostatically com-

pressed at a pressure of 20000 psi (1400 kg/cm²) to produce a cladding having a density of 1.85 g/cc. High pressure isostatic compression joined the ring segments into a continuous coating about 1/4 inch (6.3 mm.) in thickness.

EXAMPLE 12

Another portion of the vermicular graphite prepared in accordance with Example 12 was radially compressed under a force of 300 psi (21 kg/cm²) into a cylindrical form having a density of 0.65 g/cc. The cylinder thus produced was then isostatically compressed under a force of 35000 psi (2450 kg/cm²) to form a cylindrical compact having a density of 1.87 g/cc. and a resistivity of 145 microhm-inches (368 microhm-cm.) in the longitudinal axis.

Two electrolytic cells were prepared to produce magnesium from a standard molten MgCl₂ bath at 750°C. The cells were operated under identical conditions except that the anode prepared in this example was employed as the anode in one such cell and a standard electrographite anode was employed in the other cell. After 159 ampere-hours the anodes were removed and weighed. The compressed vermicular graphite anode was found to have lost only 0.059 g. per g. of magnesium produced whereas the electrographite had lost 0.096 g. per g. of magnesium produced.

WHAT WE CLAIM IS:—

1. A process for producing a graphite structure which comprises compressing vermicular graphite, the compression being effected in at least two steps, the compression of the first step being along at least one axis and the compression of the second step being along at least one other axis perpendicular to said first axis or at least one of said first axes.

2. A process according to claim 1 wherein the vermicular graphite employed has an apparent bulk density of from 0.0016 to 0.16 g/cc.

3. A process as claimed in claim 1 wherein the vermicular graphite employed has an apparent bulk density of from 0.0032 to 0.032 g/cc.

4. A process as claimed in any one of claims 1 to 3 wherein the pressure applied in carrying out either step of the compression of the vermicular graphite is up to 3500 kg/cm² (gauge).

5. A process as claimed in any one of claims 1 to 4 wherein the pressure applied in carrying out either step of the compression of the vermicular graphite is at least 3.5 kg/cm² (gauge).

6. A process as claimed in any one of claims 1 to 5 wherein the pressure applied in carrying out the compression of the vermicular

cular graphite is sufficient to produce a final bulk density of from 0.3 to 2.0 g/cc.

7. A process as claimed in any one of Claims 1 to 6 wherein the vermicular graphite is blended with from 2 to 55 weight percent, based on combined weight, of a bonding agent prior to compressing the graphite.

8. A process as claimed in Claim 7 wherein the bonding agent is a polymer of ethylene, styrene, an ethylenically unsaturated chloride, an epoxide, or tetrafluoroethylene, a polyester, or a phenol-formaldehyde resin.

9. A process as claimed in Claim 7 wherein the bonding agent is an inorganic vitreous glass-forming material which contains one or more of boric oxide, silica, phosphorus pentoxide, a germanium oxide, vanadium pentoxide, and beryllium fluoride.

10. A process as claimed in Claim 7 wherein the bonding agent is a glass-forming composition containing at least two oxides selected from silica, aluminum oxide, sodium oxide, potassium oxide, magnesium oxide, cuprous oxide, barium oxide, lead oxide, and boric oxide.

11. A process as claimed in Claim 7 wherein the bonding agent is a char-yielding substance and the compressed blend of vermicular graphite and bonding agent is heated at temperature within the range of from 800 to 1200°C. until volatiles are substantially removed.

12. A process as claimed in Claim 11 wherein the char-yielding substance comprises asphalt, tar, sugar, phenolformaldehyde resin, coal tar pitch, a saccharide, polyvinylidene chloride or a copolymer containing polyvinylidene chloride.

13. A process according to any one of Claims 7 to 12 wherein the bonding agent is a powder having a particle size less than 0.149 mm.

14. A process as claimed in any one of Claims 1 to 6 wherein the vermicular graphite is blended with from 0.5 to 10 weight percent, based on combined weight, of an oxidation retardant selected from the oxides of boron and phosphorus and metal borates and phosphates and mixtures thereof.

15. A process as claimed in any one of Claims 1 to 3 wherein structures suitable for electrodes in electrolysis of aqueous solutions are produced by compressing the vermicular graphite along one axis to produce a compact and then compressing the compact along an axis substantially perpendicular to the original compression axis to a density of at least 1.4 g/cc.

16. A process as claimed in Claim 15 wherein the compressing along one axis is to a density of from 0.2 to 1.0 g/cc.

17. A process as claimed in Claim 15 wherein the compressing along one axis to

form a compact and the compressing along an axis perpendicular to the original axis are repeated sequentially.

18. A process as claimed in any one of Claims 15 to 17 wherein the final compression is to a density of from 1.7 to 2.0 g/cc.

19. A process as claimed in Claim 15 or 16 wherein the compressing of the compact along an axis substantially perpendicular to the original compression axis is to a density of about 1.4 g/cc. and the structure thus formed is compressed isostatically to a density of from 1.7 to 2.0 g/cc.

20. A process as claimed in any one of Claims 15 to 23 wherein the vermicular graphite is blended with from 1 to 25 weight percent, based on combined weight, of a bonding agent.

21. A process as claimed in Claim 20 wherein the bonding agent is polyethylene.

22. A process as claimed in Claim 20 wherein the bonding agent is phenol-formaldehyde resin.

23. A process as claimed in any one of Claims 15 to 19 wherein the vermicular graphite is blended with from 1 to 25 weight percent, based on combined weight, of a bonding agent which functions on the application of heat and the finally compressed structure is heated to activate the bonding agent.

24. A process as claimed in any one of Claims 1 to 3 wherein the vermicular graphite is initially compressed in one axis or radially under sufficient pressure to form an integral structure having a density of at least 0.25 g/cc and the integral structure thus formed is compressed isostatically to a density of at least 1.5 g/cc.

25. A process as claimed in Claim 24 wherein the initial compression is sufficient to form an integral structure having a density of from 0.5 to 0.7 g/cc.

26. A process as claimed in Claim 24 or 25, wherein the initial compression is carried out at a pressure of from 14 to 21 kg/cm² (gauge).

27. A process as claimed in any one of Claims 24 to 26 wherein the isostatic compression is carried out at a pressure of from 245 to 3500 kg/cm² (gauge).

28. A process as claimed in any one of Claims 24 to 27 wherein prior to carrying out the initial compression the vermicular graphite is placed surrounding at least a portion of an electrolytic graphite core and the initial compression is radial.

29. A process as claimed in Claim 28 wherein prior to placing the vermicular graphite surrounding the core the vermicular graphite is compressed uniaxially to form an integral structure having a density of from 0.015 to 0.10 g/cc.

30. A process as claimed in Claim 1 sub-

stantially as described herein with reference
to the foregoing examples.

31. Graphite structures whenever pro-
duced by the process of any one of Claims
5 1 to 30.

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